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Thermal Conductivity of Carbon Tetrafluoride with Argon and Helium

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The paper presents new measurements of the thermal conductivity of the binary mixtures of carbon tetrafluoride with helium and argon. Measurements were performed in a transient, hot-wire instrument at a nominal temperature of 27.5°C and over a range of densities (pressure up to 12 MPa). The accuracy is estimated to be 0.4%, deteriorating to 0.7% around the critical density. The paper provides polynomial fits which represent the data with a standard deviation of 0.4%. An analysis in terms of the Monchick–Pereira–Mason theory, with the translational contributions computed on the basis of earlier measurements of the viscosity of these mixtures, leads to a reasonable representation of the composition dependence of the zero-density thermal conductivity; the collision numbers ζ_{ij} are treated here as adjustable parameters to obtain an optimum fit for each mixture.

KEY WORDS: argon mixture; carbon tetrafluoride mixtures; helium mixture; statistical mechanics; thermal conductivity.

1. INTRODUCTION

Extending our program of providing high-precision data on the thermal conductivity of binary gaseous mixtures [1–6], we have performed measurements on the two binary mixtures of carbon tetrafluoride with helium and argon, respectively. We have here mixtures of a polyatomic gas which is thought of as consisting of spherical molecules whose vibrational modes are excited even at room temperature. This, then, is a pair of mixtures of two monatomic molecules, with the heaviest molecule of the most complex structure in our series.

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To facilitate an analysis of our results in terms of statistical mechanics, we have at our disposal high-quality data on the viscosity of the same mixtures in the limit of zero density [7].

2. EXPERIMENTAL

The measurements were performed in our transient, hot-wire instrument; the procedures used for data reduction were identical with those used in the past [8]. The mixtures were prepared gravimetrically with helium and argon of 99.99% purity or better and with 99.7% pure CF_4. All measurements were performed at a nominal temperature of 27.5°C within the pressure range 0.7–12 MPa. The density of CF_4 was taken from the work of D. R. Douslin et al. [9]. The density of the mixtures was determined directly by us, as in the past [10].

3. RESULTS

The program covered the following molar compositions: He-CF_4, $x_{He} = 0$; 0.2785; 0.4812; 0.8047; 0.9045, Ar-CF_4, $x_{Ar} = 0.3216$; 0.6007; 0.8450. The data for pure helium and argon were taken from Ref. 8.

The results of check measurements on argon and nitrogen are seen plotted in Fig. 1. The reference values for argon and nitrogen were calculated

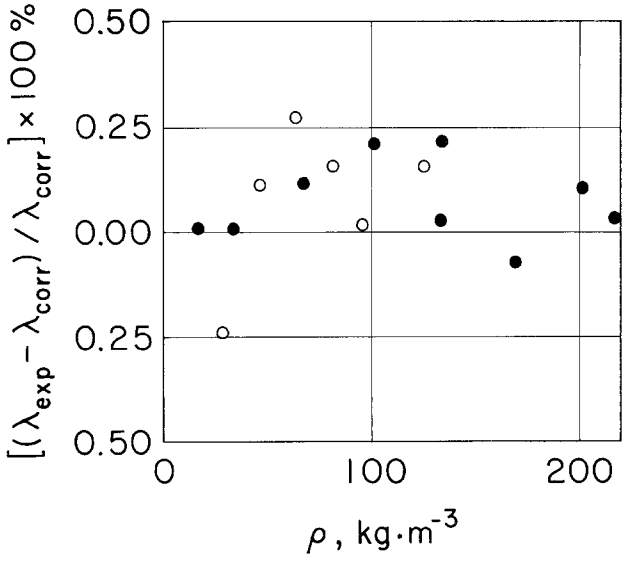

Fig. 1. Deviation plot for check measurements. (●) Ar; (○) N_2.

with the aid of the correlations in Refs. 8 and 11, respectively. The maximum deviation from previous measurements did not exceed 0.3%.

The new data for pure CF_4 and its mixtures are listed in Tables I–IX; they have all been reduced to the nominal temperature of 27.5°C with the aid of the correction factors $(\partial\lambda/\partial T)_{27.5°C}$ indicated in each table and assumed independent of density [1, 10]. In the case of CF_4, the nominal temperature of 27.5°C (300.65 K) is fairly close to the critical temperature of $T_{cr} = 227.6$ K and the maximum density of $\rho = 750\ \text{kg} \cdot \text{m}^{-3}$ exceeds the critical density $\rho_{cr} = 629\ \text{kg} \cdot \text{m}^{-3}$. For these reasons the use of a uniform linear correction becomes somewhat questionable and may affect the accuracy in part of our range by as much as an additional 0.3%.

4. ANALYSIS

The normalized values were subjected to the statistical analysis described earlier in Ref. 12. The coefficients of the virial expansion

$$\lambda = c_0 + c_1\rho + c_2\rho^2 + \cdots, \tag{1}$$

Table I. Thermal Conductivity of Carbon Tetrafluoride, Series 1, $T_{nom} = 27.5$°C

Pressure, P (MPa)	Equilibrium temperature, T_0 (°C)	Density at equil. temp., $\rho_0(P, T_0)$ (kg·m^{-3})	Reference temperature, T_r (°C)	Density at ref. temp., $\rho_r(P, T_r)$ (kg·m^{-3})	Thermal conductivity $\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	Thermal conductivity $\lambda(T_{nom}, \rho_r)$ (mW·m^{-1}·K^{-1})
0.9750	23.89	36.02	28.01	35.46	16.51	16.46
1.55	23.90	58.59	28.00	57.61	16.79	16.75
2.02	23.86	77.59	28.08	76.16	17.05	17.01
2.59	23.84	101.9	28.05	99.84	17.40	17.36
3.27	23.85	132.6	28.12	129.6	18.03	17.98
3.96	23.82	165.1	28.08	161.1	18.77	18.72
4.52	23.83	193.1	28.38	187.7	19.33	19.26
5.06	23.84	221.5	28.36	215.0	20.05	19.98
5.72	23.86	257.3	28.30	249.1	20.86	20.80
6.29	23.82	289.9	28.41	279.7	21.65	21.57
6.29	23.82	289.9	28.10	280.4	21.60	21.55
7.12	23.84	339.4	28.39	326.6	22.88	22.81
7.80	23.86	281.0	28.41	365.7	24.08	24.01
8.52	23.85	425.6	28.41	407.8	25.30	25.23
9.13	23.88	463.1	28.42	443.4	26.38	26.31
9.29	23.89	472.8	28.38	452.8	26.59	26.52
10.0	23.92	516.1	28.43	493.9	27.90	27.82
10.5	23.91	543.6	28.46	520.2	28.56	28.48
11.0	23.92	572.0	28.46	547.5	29.42	29.35

$(\delta\lambda/\partial T)_{27.5°C} = 0.079$ mW·m^{-1}·K^{-2}

Table II. Thermal Conductivity of Carbon Tetrafluoride, Series 2, $T_{nom} = 27.5°C$

Pressure, P (MPa)	Equilibrium temperature, T_0 (°C)	Density at equil. temp., $\rho_0(P, T_0)$ (kg·m^{-3})	Reference temperature, T_r (°C)	Density at ref. temp., $\rho_r(P, T_r)$ (kg·m^{-3})	Thermal conductivity $\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	Thermal conductivity $\lambda(T_{nom}, \rho_r)$ (mW·m^{-1}·K^{-1})
0.9075	23.67	33.471	26.64	33.097	16.35	16.42
1.246	23.69	46.55	26.61	46.02	16.57	16.64
1.65	23.71	62.66	26.61	61.91	16.82	16.89
2.16	23.71	83.50	26.58	82.43	17.15	17.22
2.76	23.72	109.4	26.62	107.8	17.57	17.64
3.20	23.71	129.4	26.55	127.5	17.95	18.02
3.75	23.72	155.3	26.61	152.7	18.47	18.54
4.33	23.74	183.8	26.55	180.7	19.01	19.08
4.75	23.69	205.1	26.55	201.4	19.47	19.54
5.48	23.71	244.5	26.55	239.6	20.55	20.62
6.04	23.69	276.0	26.55	270.1	21.28	21.36
6.60	23.63	308.9	26.51	301.7	22.21	22.28
7.10	23.62	338.9	26.51	330.5	22.91	22.99
7.87	23.64	386.1	26.51	376.0	24.25	24.33
8.67	23.59	436.0	26.49	424.0	25.70	25.78
9.45	23.62	483.9	26.49	470.4	26.98	27.06
10.16	23.66	526.3	26.51	511.7	28.36	28.44
10.88	23.64	567.6	26.48	552.1	29.48	29.56
11.60	23.66	607.3	26.51	591.0	30.73	30.81
12.06	23.64	631.5	26.52	614.7	31.39	31.47
12.60	23.64	658.7	26.58	641.2	32.26	32.34
13.09	23.64	682.0	26.62	664.2	32.89	32.96
13.64	23.68	707.4	26.67	689.2	33.76	33.82
14.11	23.62	728.5	26.69	709.8	34.42	34.49
14.64	23.59	751.0	26.75	731.7	35.23	35.29
15.24	23.57	775.3	26.81	755.6	35.93	36.10

$(\partial\lambda/\partial T)_{27.5°C} = 0.079$ mW·m^{-1}·K^{-2}

together with their standard deviations, are listed in Table X. In our range, the representations of the thermal conductivity of pure CF_4 required a polynomial of fourth degree, whereas for the mixtures it was sufficient to carry the expansion only as far as the quadratic term in density.

For interpolation purposes, we used a truncated equation with the first term in it forced to be equal to c_0 in the virial expansion of Eq. (1). Thus we put

$$\lambda = \lambda^\circ + a_1\rho + a_2\rho^2 + a_3\rho^3 + a_4\rho^4 \tag{2}$$

with

$$\lambda^\circ \equiv c_0 \tag{3}$$

The coefficients of this equation are listed in Table XI.

Table III. Thermal Conductivity of Helium–Carbon Tetrafluoride Mixture with $x_{He} = 0.2785$, $T_{nom} = 27.5°C$

Pressure, P (MPa)	Equilibrium temperature, T_0 (°C)	Density at equil. temp., $\rho_0(P, T_0)$ (kg·m^{-3})	Reference temperature, T_r (°C)	Density at ref. temp., $\rho_r(P, T_r)$ (kg·m^{-3})	Thermal conductivity $\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	Thermal conductivity $\lambda(T_{nom}, \rho_r)$ (mW·m^{-1}·K^{-1})
1.044	23.84	27.68	26.73	27.39	28.47	28.54
1.60	23.84	42.64	26.77	42.17	28.61	28.69
2.32	23.87	62.37	26.78	62.66	28.94	29.01
3.13	23.91	84.99	26.81	83.97	29.17	29.24
4.10	23.84	113.1	26.84	111.6	29.66	29.72
5.08	23.79	141.7	26.83	139.6	30.10	30.17
6.12	23.82	172.7	26.81	170.1	30.67	30.74
7.10	23.69	201.6	26.81	198.2	31.41	31.48
8.18	23.69	233.8	26.82	229.5	32.06	32.13
9.21	23.71	264.4	26.82	259.1	32.85	32.93
10.06	23.73	290.6	26.79	284.5	33.60	33.67
10.93	23.69	316.0	26.75	309.0	34.26	34.34
11.55	23.67	334.9	26.64	327.3	34.66	34.75
11.98	23.69	346.8	26.63	338.8	35.01	35.10

$(\partial\lambda/\partial T)_{27.5°C} = 0.104$ mW·m^{-1}·K^{-2}

Table IV. Thermal Conductivity of Helium–Carbon Tetrafluoride Mixture with $x_{He} = 0.4812$ at $T_{nom} = 27.5°C$

Pressure, P (MPa)	Equilibrium temperature, T_0 (°C)	Density at equil. temp., $\rho_0(P, T_0)$ (kg·m^{-3})	Reference temperature, T_r (°C)	Density at ref. temp., $\rho_r(P, T_r)$ (kg·m^{-3})	Thermal conductivity $\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	Thermal conductivity $\lambda(T_{nom}, \rho_r)$ (mW·m^{-1}·K^{-1})
1.241	24.11	23.75	26.42	23.55	42.16	42.30
1.79	24.02	34.66	26.41	34.37	42.23	42.37
2.61	24.00	50.64	26.45	50.19	42.45	42.59
3.54	24.03	68.98	26.45	68.35	42.77	42.91
4.35	24.02	85.09	26.43	84.30	43.05	43.20
5.18	24.02	101.2	26.40	100.2	43.04	43.19
6.20	23.94	121.3	26.42	120.0	43.58	43.72
7.21	23.94	140.8	26.47	139.3	43.87	44.01
8.11	24.01	157.8	26.50	156.1	44.03	44.17
8.99	23.72	175.3	26.14	173.5	44.28	44.46
9.77	23.74	190.7	26.16	188.7	44.61	44.79
10.50	23.74	204.3	26.16	202.1	44.99	45.17
11.34	23.74	219.9	26.16	217.4	45.22	45.40
12.07	23.79	233.6	26.21	231.0	45.36	45.53
12.77	23.82	256.3	26.17	253.4	45.92	46.10

$(\partial\lambda/\partial T)_{27.5°C} = 0.133$ mW·m^{-1}·K^{-2}

Table V. Conductivity of Helium–Carbon Tetrafluoride Mixture with $x_{He} = 0.8047$ at $T_{nom} = 27.5°C$

Pressure, P (MPa)	Equilibrium temperature, T_0 (°C)	Density at equil. temp., $\rho_0(P, T_0)$ (kg·m^{-3})	Reference temperature, T_r (°C)	Density at ref. temp., $\rho_r(P, T_r)$ (kg·m^{-3})	Thermal conductivity	
					$\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	$\lambda(T_{nom}, \rho_r)$ (mW·m^{-1}·K^{-1})
1.091	23.66	9.913	26.20	9.828	86.22	86.50
2.04	23.64	16.67	26.20	16.52	86.85	87.13
3.06	23.63	24.86	26.21	24.64	86.74	87.02
4.05	23.69	33.73	26.16	33.45	87.18	87.47
5.06	23.68	40.70	26.16	40.36	87.15	87.44
6.08	23.68	48.66	26.17	48.25	86.96	87.25
8.07	23.70	56.20	26.20	55.72	87.30	87.58
8.13	23.70	64.15	26.17	63.62	87.58	87.87
9.10	23.73	71.66	26.18	71.07	87.80	88.09
10.14	23.74	79.45	26.20	78.79	88.02	88.30
11.11	23.94	87.43	26.48	86.68	87.77	87.99
12.08	23.94	93.61	26.64	92.76	88.10	88.29
12.63	24.04	97.56	26.26	96.83	88.04	88.30

$(\partial\lambda/\partial T)_{27.5°C} = 0.217$ mW·m^{-1}·K^{-2}

Table VI. Thermal Conductivity of Helium–Carbon Tetrafluoride Mixture with $x_{He} = 0.9045$ at $T_{nom} = 27.5°C$

Pressure, P (MPa)	Equilibrium temperature, T_0 (°C)	Density at equil. temp., $\rho_0(P, T_0)$ (kg·m^{-3})	Reference temperature, T_r (°C)	Density at ref. temp., $\rho_r(P, T_r)$ (kg·m^{-3})	Thermal conductivity	
					$\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	$\lambda(T_{nom}, \rho_r)$ (mW·m^{-1}·K^{-1})
1.59	24.24	7.63	26.90	7.56	113.58	113.74
2.34	24.30	11.21	26.90	11.11	113.73	113.89
3.06	24.31	14.61	26.94	14.48	113.85	114.00
3.81	24.34	18.16	26.95	18.00	114.06	114.21
5.34	24.32	25.32	26.95	25.10	114.04	114.18
6.09	24.34	28.75	26.95	28.50	114.17	114.32
6.90	24.34	32.37	26.94	32.09	114.71	114.86
8.53	24.41	39.86	26.98	39.53	115.31	115.45
9.08	24.42	42.12	27.07	41.76	115.38	115.50
11.95	24.29	54.68	26.99	54.20	115.38	115.52

$(\partial\lambda/\partial T)_{27.5°C} = 0.270$ mW·m^{-1}·K^{-2}

Table VII. Thermal Conductivity of Argon–Carbon Tetrafluoride Mixture with $x_{Ar} = 0.3216$ at $T_{nom} = 27.5°C$

Pressure, P (MPa)	Equilibrium temperature, T_0 (°C)	Density at equil. temp., $\rho_0(P, T_0)$ (kg·m^{-3})	Reference temperature, T_r (°C)	Density at ref. temp., $\rho_r(P, T_r)$ (kg·m^{-3})	Thermal conductivity	
					$\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	$\lambda(T_{nom}, \rho_r)$ (mW·m^{-1}·K^{-1})
1.056	24.56	32.04	26.86	31.76	16.72	16.77
1.55	24.48	47.65	26.86	47.22	16.88	16.93
2.07	24.48	64.34	26.86	63.74	17.23	17.27
2.58	24.48	80.58	26.89	79.79	17.44	17.48
3.10	24.58	97.93	26.89	96.97	17.72	17.77
3.59	24.58	114.8	26.90	113.6	18.12	18.17
4.07	24.56	132.4	26.88	131.0	18.46	18.50
4.85	24.52	160.2	26.87	158.3	18.99	19.04
5.60	24.51	188.5	26.84	186.2	19.59	19.64
6.29	24.45	214.7	26.79	211.9	20.33	20.38
6.29	24.45	314.7	26.79	211.9	20.13	20.18
7.05	24.46	243.5	26.80	240.1	21.01	21.06
7.89	24.48	277.4	26.83	273.1	21.81	21.85
8.60	24.53	305.1	26.85	300.9	22.47	22.52
9.06	24.56	324.6	26.88	318.9	23.17	23.21

$(\partial\lambda/\partial T)_{27.5°C} = 0.072$ mW·m^{-1}·K^{-2}

Table VIII. Thermal Conductivity of Argon–Carbon Tetrafluoride Mixture with $x_{Ar} = 0.6007$ at $T_{nom} = 27.5°C$

Pressure, P (MPa)	Equilibrium temperature, T_0 (°C)	Density at equil. temp., $\rho_0(P, T_0)$ (kg·m^{-3})	Reference temperature, T_r (°C)	Density at ref. temp., $\rho_r(P, T_r)$ (kg·m^{-3})	Thermal conductivity	
					$\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	$\lambda(T_{nom}, \rho_r)$ (mW·m^{-1}·K^{-1})
0.7917	24.54	19.12	26.91	18.96	17.17	17.21
1.31	24.54	32.08	26.86	31.81	17.31	17.35
1.85	24.49	45.40	26.78	45.02	17.57	17.61
2.32	24.36	57.33	26.77	56.83	17.79	17.83
2.87	24.37	71.46	26.76	70.82	18.06	18.10
3.49	24.40	87.73	26.76	86.94	18.32	18.37
4.28	24.38	109.0	26.75	108.0	18.62	18.67
5.31	24.37	137.1	26.75	135.8	19.23	19.28
6.10	24.40	159.3	26.75	157.7	19.79	19.84
7.12	24.37	187.6	26.74	185.7	20.32	20.37
8.10	24.40	215.7	26.74	213.3	21.03	21.08
9.14	24.44	246.0	26.73	243.3	21.91	21.96
10.15	24.40	275.6	26.68	272.4	22.65	22.70
11.20	24.32	304.8	26.60	301.1	23.41	23.47
12.11	24.35	332.4	26.51	328.4	24.27	24.33
12.59	24.34	346.1	26.48	341.9	24.61	24.68

$(\partial\lambda/\partial T)_{27.5°C} = 0.064$ mW·m^{-1}·K^{-2}

Table IX. Termal Conductivity of Argon–Carbon Tetrafluoride Mixture with $x_{Ar} = 0.8450$ at $T_{nom} = 27.5°C$

Pressure, P (MPa)	Equilibrium temperature, T_0 (°C)	Density at equil. temp., $\rho_0(P, T_0)$ (kg·m^{-3})	Reference temperature, T_r (°C)	Density at ref. temp., $\rho_r(P, T_r)$ (kg·m^{-3})	Thermal conductivity $\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	Thermal conductivity $\lambda(T_{nom}, \rho_r)$ (mW·m^{-1}·K^{-1})
0.8508	24.08	16.43	26.46	16.30	17.71	17.77
1.16	24.08	22.39	26.46	22.21	17.85	17.91
1.54	24.08	30.06	26.44	29.81	17.95	18.02
2.23	24.11	44.53	26.48	44.16	18.12	18.18
3.05	24.08	60.04	26.42	59.52	18.50	18.57
3.58	24.05	70.69	26.42	70.06	18.73	18.80
4.35	24.05	86.59	26.41	85.82	18.94	19.01
5.36	23.98	107.8	26.39	106.7	19.46	19.52
6.32	23.96	127.8	26.39	126.6	19.91	19.98
7.25	23.95	147.4	26.39	145.9	20.41	20.47
8.04	23.93	163.9	26.39	162.2	20.91	20.98
8.94	23.93	184.6	26.39	182.6	21.48	21.54
9.79	23.95	202.5	26.40	200.3	21.84	21.90
10.60	24.02	219.5	26.40	217.2	22.44	22.50
11.38	24.03	236.3	26.42	233.7	23.00	23.06
12.16	24.09	253.2	26.42	250.4	23.36	23.42

$(\partial\lambda/\partial T)_{27.5°C} = 0.060$ mW·m^{-1}·K^{-2}

The deviation plots in Figs. 2–4 demonstrate that the maximum deviation of the measured data from the appropriate equation is ±0.6% with a standard deviation of ±0.4%.

5. COMPARISON WITH RESULTS OF OTHER AUTHORS

Reference 8 contains a comparison of our results for He and Ar with those of other authors. As far as pure CF_4 is concerned, we could discover only three publication [13–15].

S. Oshen et al. [13] and B. M. Rosenbaum and G. Thodos [14] made measurements in a coaxial-cylinder apparatus and covered the range of temperatures 6.7–160°C and pressures 0.37–69 MPa. J. D. Lambert et al. [15] made a single measurement at 66°C and 0.1 MPa in a steady-state hot-wire apparatus. At zero density, the application of a linear temperature correction with $(\partial\lambda/\partial T)_{27.5°C} = 0.079$ mW · m^{-1} · K^{-2} yields the following comparison at 27.5°C:

Table X. Statistical Analysis of the Experimental Results, Based on Eq. (1)

System	ρ' ($kg \cdot m^{-3}$)	$c_0 \pm \sigma(c_0)$ ($mW \cdot m^{-1} \cdot K^{-1}$)	$c_1 \pm \sigma(c_1)$ ($\mu W \cdot m^2 \cdot kg^{-1} \cdot K^{-1}$)	$c_2 \pm \sigma(c_2)$ ($nW \cdot m^5 \cdot kg^{-2} \cdot K^{-1}$)	$c_3 \pm \sigma(c_3)$ ($pW \cdot m^8 \cdot kg^{-3} \cdot K^{-1}$)	$c_4 \pm \sigma(c_4)$ ($fW \cdot m^{11} \cdot kg^{-4} \cdot K^{-1}$)	σ_λ (%)
CF_4	76	15.99 ± 0.06	13.71 ± 1.2	—	—	—	0.28
	250	16.03 ± 0.05	11.04 ± 0.8	33.2 ± 3.0	—	—	0.32
	494	16.05 ± 0.04	10.08 ± 0.7	44.1 ± 3.4	−33 ± 4	—	0.31
	732	16.10 ± 0.05	8.70 ± 1.0	55.1 ± 5.8	−65 ± 12	31 ± 9	0.34
He–CF_4							
$x_{He} = 0.2785$	85	28.18 ± 0.05	12.78 ± 0.9	—	—	—	0.13
	312	28.28 ± 0.04	8.83 ± 0.6	35.2 ± 1.7	—	—	0.15
$x_{He} = 0.4812$	85	41.88 ± 0.06	15.09 ± 1.1	—	—	—	0.13
	220	42.02 ± 0.09	10.97 ± 1.7	20.9 ± 7.0	—	—	0.20
$x_{He} = 0.8047$	97	86.62 ± 0.12	18.28 ± 1.9	—	—	—	0.22
$x_{He} = 0.9045$	54	113.33 ± 0.20	45.18 ± 4.5	—	—	—	0.22
Ar–CF_4							
$x_{Ar} = 0.3216$	97	16.24 ± 0.05	15.66 ± 0.8	—	—	—	0.48
	350	16.29 ± 0.07	13.08 ± 1.0	27.1 ± 3.5	—	—	0.55
$x_{Ar} = 0.6007$	45	16.89 ± 0.09	15.50 ± 0.3	—	—	—	0.28
	332	16.92 ± 0.04	14.01 ± 0.5	25.0 ± 1.5	—	—	0.28
$x_{Ar} = 0.8450$	86	17.47 ± 0.04	18.09 ± 0.8	—	—	—	0.30
	234	17.53 ± 0.04	14.61 ± 0.9	38.4 ± 3.3	—	—	0.31

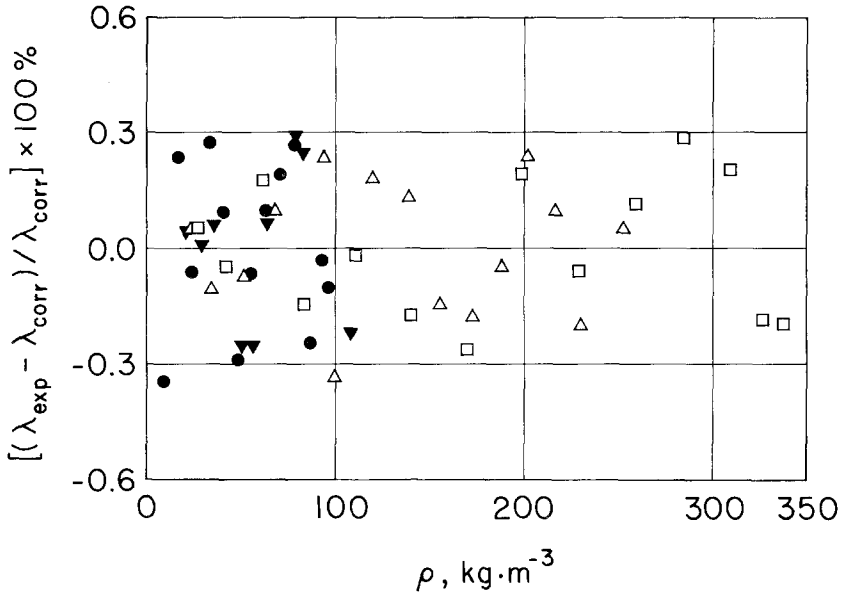

Fig. 2. Deviation of masured data from polynomial correlation, Eq. (2). (●) Series 1, $T_r = 28°C$; (○) series 2, $T_r = 26°C$.

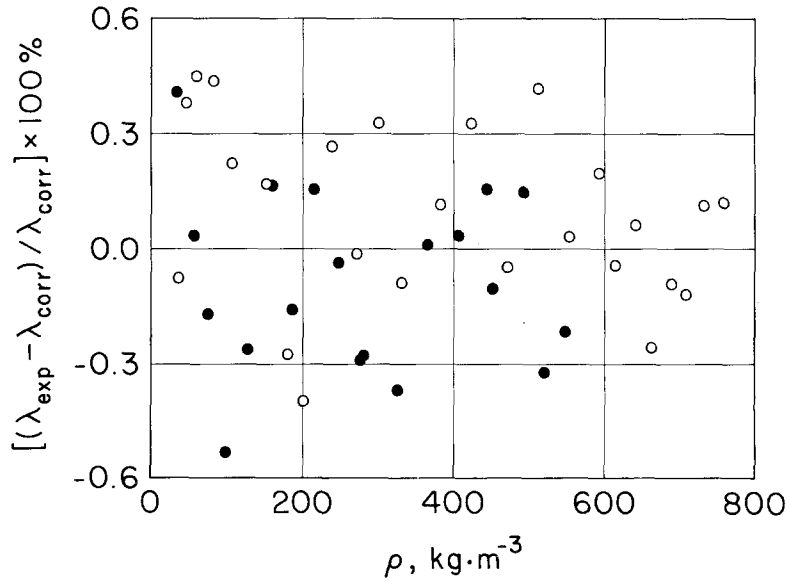

Fig. 3. Deviation of measured data from polynomial correlations, Eq. (2). CF_4–He mixtures. x_{He}: (□) 0.2785; (△) 0.4812; (●) 0.8047; (▼) 0.9045.

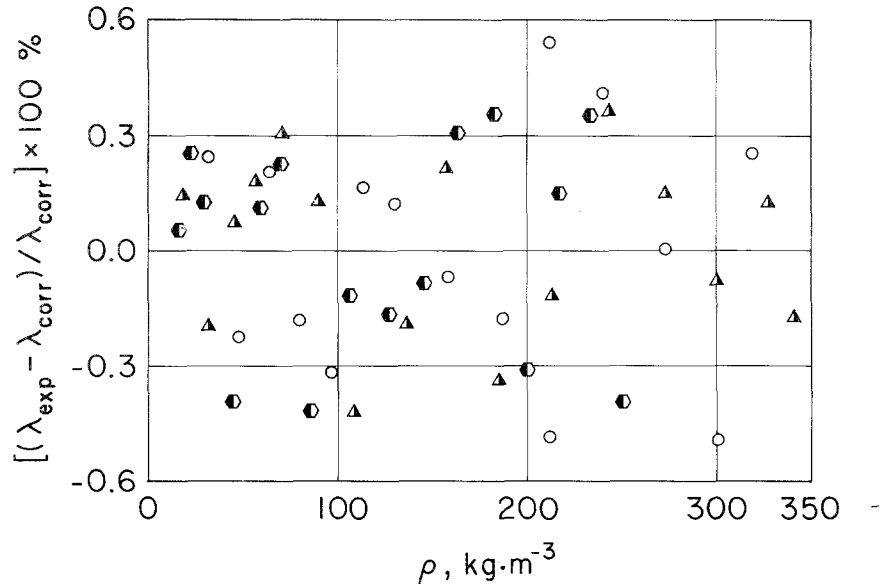

Fig. 4. Deviation of measured data from polynomial correlation, Eq. (2). CF_4–Ar mixtures. x_{Ar}: (○) 0.3216; (▲) 0.6007; (◐) 0.8450.

$\lambda^\circ = 16.15$ mW · m^{-1} · K^{-1} in Ref. 13,

$\lambda^\circ = 15.72$ mW · m^{-1} · K^{-1} in Ref. 14, and

$\lambda = 15.95$ mW · m^{-1} · K^{-1} in Ref. 15 (at 0.1 MPa),

with $\lambda^\circ = 16.03$ mW · m^{-1} · K^{-1} in Table XI,

or differences of +0.75%, −1.93%, and −0.50%, respectively.

In order to compare the difference in the density effects reported by us and by Thodos et al. [13, 14], we have plotted the excess thermal conductivity

$$\Delta\lambda = \lambda(T, \rho) - \lambda^\circ(T)$$

against density in Fig. 5. In the comparison we ignored the dependence of $\Delta\lambda$ on temperature because it is likely to be small in the range 6.7–41.7°C covered by the graph. The introduction of a correction to reduce all data to a common temperature would necessarily be questionable and thus not justified in this case.

Given the differences in precision, the agreement has turned out to be acceptable. At the higher temperatures, however, the data in Ref. 14 suggest that the excess thermal conductivity, $\Delta\lambda$, is not a unique function of density.

Table XI. The Coefficients of the Correlation, Eq. (2)

System	λ° ($mW \cdot m^{-1} \cdot K^{-1}$)	a_1 ($\mu W \cdot m^2 \cdot kg^{-1} \cdot K^{-1}$)	a_2 ($nW \cdot m^5 \cdot kg^{-2} \cdot K^{-1}$)	a_3 ($pW \cdot m^8 \cdot kg^{-3} \cdot K^{-1}$)	a_4 ($fW \cdot m^{11} \cdot kg^{-4} \cdot K^{-1}$)	σ_λ (%)
He CF_4						
$x_{He} = 0$	16.03	9.625	51.98	−62.19	30.4	0.35
$x_{He} = 0.2785$	28.23	9.914	31.17	—	—	0.21
$x_{He} = 0.4812$	42.00	11.49	18.14	—	—	0.18
$x_{He} = 0.8047$	86.62	18.28	—	—	—	0.22
$x_{He} = 0.9045$	113.3	45.18	—	—	—	0.22
Ar–CF_4						
$x_{Ar} = 0.3216$	16.27	13.56	25.17	—	—	0.51
$x_{Ar} = 0.6007$	16.90	14.48	24.57	—	—	0.28
$x_{Ar} = 0.8450$	17.50	15.57	33.74	—	—	0.34

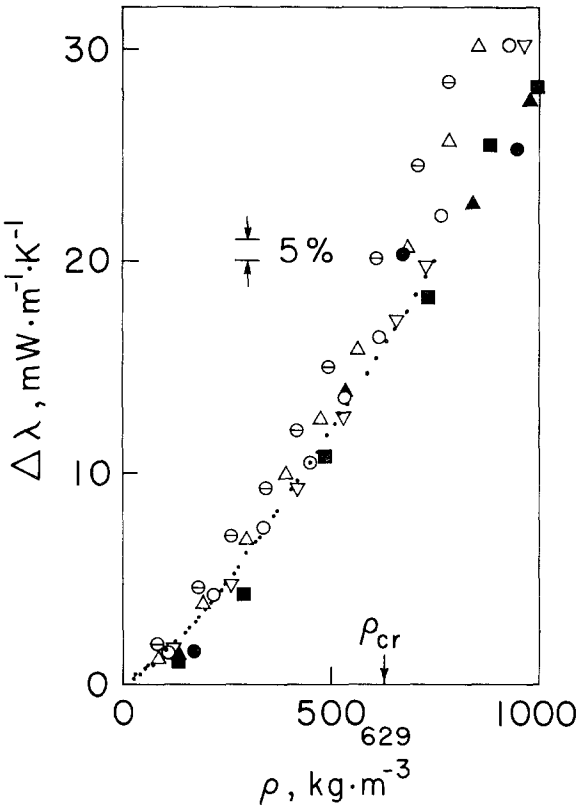

Fig. 5. Excess thermal conductivity of CF_4. (·) Present measurements (27.5°C); (●) 6.7°C [13]; (▲) 23.8°C [13]; (■) 41.7°C [13]; (▽) 62.8°C [14]; (○) 98.7°C [14]; (△) 128.4°C [14]; (⊖) 160.9°C [14].

6. DISCUSSION

6.1. Zero Density

We analyze our experimental results for the mixtures by following the same sequence of steps as in Refs. 1–3. Table XII lists the values of the various input data employed in the calculation and the sources for them. The rotational relaxation number for CF_4 was estimated with the aid of the model proposed by Wang-Chang and Uhlenbeck [16]. The value of $D_{i,\mathrm{int},i}/D_{ii}$ was treated as a free parameter whose value (0.96) was chosen to secure a best fit to the formula derived by L. A. Viehland et al. [17] and J. A. R. Coope and R. F. Snider [18].

Table XII. Quantities Employed for the Calculation of the Thermal Conductivity of Mixtures at 27.5°C

	CF_4–CF_4	CF_4 – He	He–He	CF_4–Ar	Ar–Ar
λ_i°(mW·m^{-1}·K^{-1})	16.03	—	155.86 [8]	—	17.74 [8]
η_i (μPa·s) [7]	17.50	11.29	19.97	19.01	22.75
$\lambda_{i(\text{mon})}$ (wW·m^{-1}·K^{-1})	6.20	45.97	155.86	10.79	17.74
C_{int}/R [25]	4.91	—	0	—	0
C_{rot}/R	1.50	—	0	—	0
ζ_{rot}	4	$\zeta_{\text{CF4–He}} = \zeta_{\text{He–CF4}} = \infty$	∞	$\zeta_{\text{Ar–CF4}} = \infty$, $\zeta_{\text{CF4–Ar}} = 40$	∞
ζ_{vib} [26]	2220.		∞		∞
A_{ij} [27]	1.094	1.123	1.127	1.093	1.092
B_{ij} [27]	—	1.103	—	1.122	—
$D_{i,\text{int},j}/D_{ij}$	0.96	1.0	1.0	1.0	1.0
$(\Delta\lambda\|\|/\lambda)_{\text{sat}}$ [28]	−0.0028	—	0	—	0
γ_{ij}(m^3·mol^{-1})	1.80×10^{-4}	6.32×10^{-5}	1.25×10^{-5}	1.05×10^{-4}	5.43×10^{-5}

In order to compare the results fo mixtures with theory, we have employed the theory due to L. Monchick et al. [19] using the input data listed in Table XII. In this calculation we left the value of the collision number ζ_{ij} adjustable. The optimum value of this quantity for both mixtures has turned out to be

$$\zeta_{ij} = \infty \text{ for } CF_4\text{–He and } \zeta_{ij} = 40 \text{ for } CF_4\text{–Ar}$$

The diagrams in Figs. 6 and 7 compare our zero-density results, λ°, for the mixtures with calculations.

The diagram in Fig. 6 refers to helium. As observed before in the case of a mixture with helium [2, 5], the application of the simpler Hirschfelder–Eucken formula [20] underestimates the thermal conductivity by as much as 5% (at $x_{He} = 0.3$); the scale of the grid in the figure tends to obscure this fact. The results of a fully inelastic calculation based on Ref. 19 are larger by

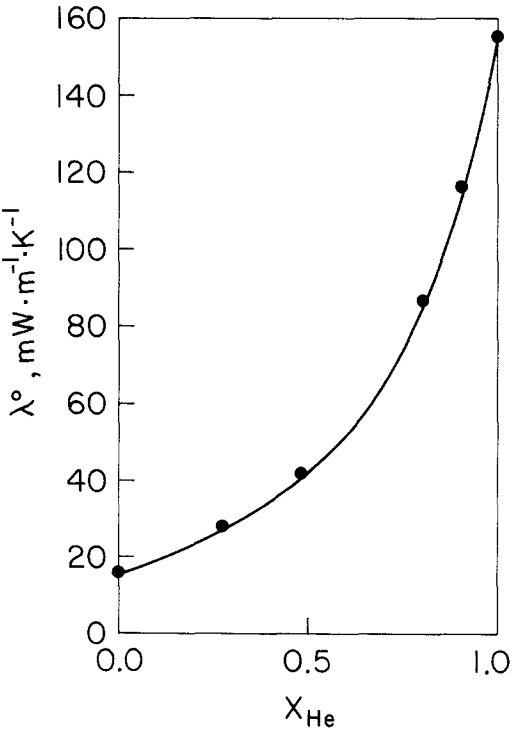

Fig. 6. Zero-density thermal conductivity of CF_4—He mixtures at 27.5°C as a function of mol fraction. (——) Fully inelastic calculation with $\zeta_{ij} = \infty$; (●) experimental results.

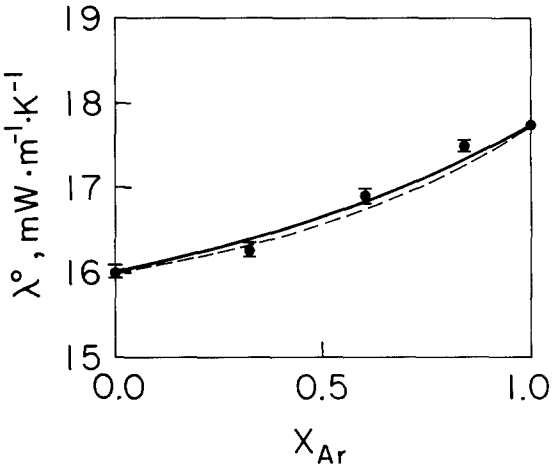

Fig. 7. Zero-density thermal conductivity of CF_4–Ar mixtures at 27.5°C as a function of mol fraction. (——) Fully inelastic calculation with $\zeta_{ij} = 40$; (– – –) Hirschfelder–Eucken equation; (●) experimental results.

not more than 0.7%. Thus, the two curves have turned out to be indistinguishable in Fig. 6.

The result for mixtures with argon, shown in Fig. 7, is much closer to experiment, the maximum deviation being one of 1.2%. A calculation which fully accounts for inelastic collisions yields values which are larger by no more than 0.6% compared with the Hirschfelder–Eucken equation.

6.2. High Density

A direct comparison with the theory developed in Refs. 21 and 22 has proved to be impossible because, as already observed for mixtures with CO_2[5] and CH_4[2, 23], the pseudoradial distribution function assumes fractional values over most of the density range. For this reason, we can compare only the initial slope

$$c_1 = (\partial\lambda/\partial\rho)_T \qquad \text{as} \quad \rho \to 0 \tag{5}$$

with the formulas of Refs. 21 and 22. This has been done in Figs. 8 and 9 for the two mixtures. In all cases, the values of the virial coefficients are those of J. H. Dymond and E. B. Smith [24]. The resulting values of γ_{ij} have been included in Table XII. The results appear to be in no more than qualitative agreement.

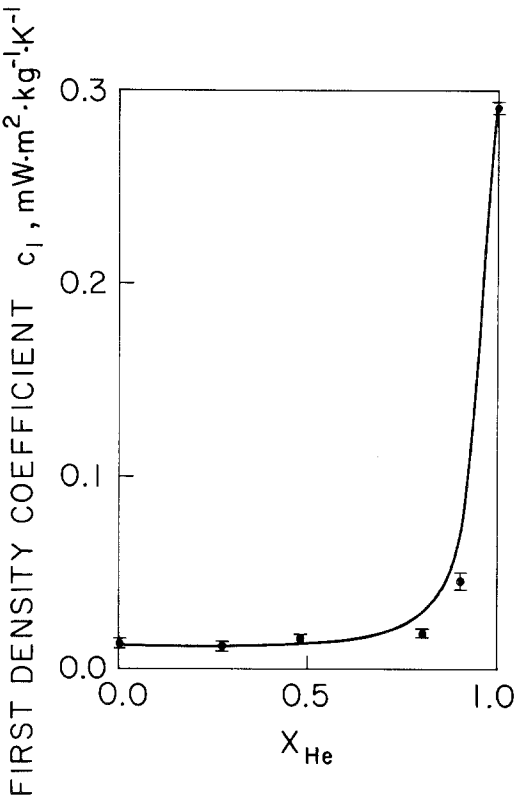

Fig. 8. Initial slope $(\partial\lambda/\partial\rho)_T$ as $\rho \to 0$ of density dependence for CF_4–He mixtures. Theory from Refs. 21 and 22.

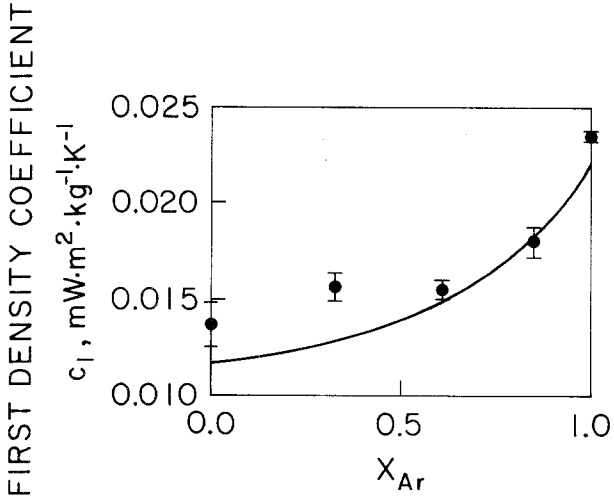

Fig. 9. Initial slope $(\partial\lambda/\lambda\rho)_T$ as $\rho \to 0$ of density dependence for CF_4–Ar mixtures. Theory from Refs. 21 and 22.

ACKNOWLEDGMENTS

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REFERENCES

1. A. A. Clifford, R. Fleeter, J. Kestin, and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **84**:18 (1980).
2. R. Fleeter, J. Kestin, R. Paul, and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **85**:215 (1981).
3. R. Fleeter, J. Kestin, R. Paul, and W. A. Wakeham, *Physica* **108A**:371 (1981).
4. R. Fleeter, J. Kestin, Y. Nagasaka, I. R. Shankland, and W. A. Wakeham, *Physica* **111A**:404 (1982).
5. J. Kestin, Y. Nagasaka, and W. A. Wakeham, *Physica* **113A**:1 (1982).
6. N. Imaishi and J. Kestin, *Physica* **126A**:98 (1984).
7. J. Kestin, H. E. Khalifa, and W. A. Wakeham, *Physica* **88A**:242 (1977).
8. J. Kestin, R. Paul, A. A. Clifford, and W. A. Wakeham, *Physica* **100A**:349 (1980).
9. D. R. Douslin, R. H. Harrison, R. T. Moore, and J. P. McCullough, *J. Chem. Phys.* **35**:1357 (1961).
10. A. A. Clifford, R. Fleeter, J. Kestin, and W. A. Wakeham, *Physica* **98A**:467 (1979).
11. N. Imaishi, J. Kestin, and W. A. Wakeham, *Physica* **123A**:50 (1984).
12. J. J. DeGroot, J. Kestin, H. Sookiazian, and W. A. Wakeham, *Physica* **92A**:117 (1978).
13. S. Oshen, B. M. Rosenbaum, and G. Thodos, *J. Chem. Phys.* **46**:2939 (1967).
14. B. M. Rosenbaum and G. Thodos, *Physica* **37**:442 (1967).
15. J. D. Lambert, K. J. Cotton, M. W. Pailthorpe, A. M. Robinson, J. Scrivins, W. R. F. Vale, and R. M. Young, *Proc. Roy. Soc. Lond.* **A231**:280 (1955).
16. C. S. Wang-Chang and G. E. Uhlenbeck, *Transport Phenomena in Polyatomic Gases* (University of Michigan Engineering Research Department, Ann Arbor, 1951).
17. L. A. Viehland, E. A. Mason, and S. I. Sandler, *J. Chem. Phys.* **68**:5277 (1978).
18. J. A. R. Coope and R. F. Snider, *J. Chem. Phys.* **70**:1075 (1979).
19. L. Monchick, A. N. G. Pereia, and E. A. Mason, *J. Chem. Phys.* **42**:3241 (1965).
20. J. O. Hirschfelder, *J. Chem. Phys.* **26**:282 (1957).
21. E. A. Mason, H. E. Khalifa, J. Kestin, R. DiPippo, and J. D. Dorfman, *Physica* **91A**:377 (1978).
22. J. Kestin and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **84**:762 (1980).
23. N. Imaishi and J. Kestin, *Physica A* (in press).
24. J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures* (Clarendon Press, Oxford, 1980).
25. Y. T. Hwang and J. J. Martin, *AIChEJ* **10**:89 (1964).
26. J. D. Lambert, *Vibrational and Rotational Relaxation in Gases* (Clarendon, Oxford, 1977).
27. G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular forces, their origin and determination* (Clarendon, Oxford, 1981).
28. L. J. F. Hermans, J. M. Koks, A. F. Hengeveld, and H. F. P. Knaap, *Physica* **50**:410 (1970)